

# HYDROGEN TRANSFER FROM CATALYST INTERMEDIATE PROTOTYPES TO STABILIZED RADICALS

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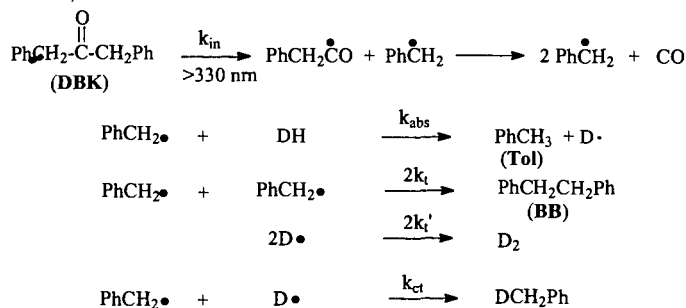
## INTRODUCTION

The transfer of hydrogen from metal-hydrogen bonds (M-H) to closed-shell molecules or free radicals, from metal-activated organic structure (MC-H) and from metal-activated heteroatom-hydrogen bonds (MS-H) are primary processes involved in catalytic hydroxylation of organic structure. The characterization of the reactivity of transition metal hydride  $\mu$ - and  $\sigma$ -bonds and agostic M-H bonds in fundamental catalysis steps is of wide interest. Whereas a substantial body of data now exists describing the kinetics of reactions of alkyl organic free radicals with main group hydrides (e.g., S-H<sup>1</sup>, Se-H<sup>2</sup>, Sn-H and Si-H<sup>3</sup>), few kinetic studies of the reactions of transition metal hydrides<sup>4</sup>, and particularly hydrides involving novel metal bonding arrangements, exist. Relatively few kinetic studies of the reaction of benzylic radicals with either main group or transition metal hydrides exist. In previous work we have determined families of basis rate expressions for abstraction of hydrogen atom by alkyl and benzylic radicals from a variety of hydrogen donors for use in competition kinetic studies to measure rate constants for homolytic molecular rearrangements related to coal and biomass hydroxylation.<sup>5</sup> Recently, we have carried out kinetic studies to determine the homolytic hydrogen transfer properties of hydrogen bonded in novel arrangements in metal clusters and other catalyst related systems. In this paper, we review recent results from application of competition kinetic methods to determination of absolute rates of abstraction of hydrogen atom from M-H, C-H and S-H bonds to the benzyl radical, where M = Mo, Os, Ru, Ir, and Rh.

## KINETIC APPROACH

The kinetic method used in studies in this laboratory to determine rates of reaction of stabilized organic free radicals makes use of the competition of self-termination of the radical of interest with abstraction of hydrogen from the donor (DH) of interest. The competition of self-termination of benzyl radical to form bibenzyl (BB) versus hydrogen abstraction to form toluene (Tol) is depicted in Scheme 1. Thus, photolysis of a convenient photoprecursor (DBK) to form benzyl radical under conditions of constant rate of photolysis of DBK is followed by abstraction of hydrogen to form toluene ( $k_{abs}$ ) versus self-termination ( $2k_t$ ) to form bibenzyl.

**Scheme 1**



The rate of formation of bibenzyl and toluene are given by the differential equations ( $[\text{PhCH}_2\bullet] = [\text{B}\bullet]$ ):

$$\frac{d[\text{Tot}(t)]}{dt} = k_{\text{abs}}[\text{DH}(t)][\text{B}\bullet] \quad (1)$$

$$\frac{d[\text{BB}(t)]}{dt} = k_t[\text{B}\bullet]^2 \quad (2)$$

Note that for constant benzyl radical concentration and short extent of consumption of donor, DH, integration of eq 1 and eq 2 yield expressions that are linear in toluene and bibenzyl with time.

Combining eqs 1 and 2, for  $\text{DH}(t) = \text{DH}(0) - \text{Tot}(t)$  leads to eqs 3 and 4:

$$\int \left( \frac{d[\text{Tot}(t)]}{[\text{DH}(0)] - [\text{Tot}(t)]} \right) = k_{\text{abs}} \sqrt{\frac{1}{k_t} [\text{BB}] \Delta t} \quad (3)$$

$$\text{Tot}(t) = \text{DH}_0 \left( 1 - e^{-\frac{k_{\text{abs}}(\sqrt{\text{BB}} \sqrt{\Delta t})}{\sqrt{k_t}}} \right) \quad (4)$$

Eq. 4 provides the time dependence of formation of toluene in terms of self-termination product, bibenzyl (BB), the elapsed time of the photolysis in seconds ( $\Delta t$ ), the initial hydrogen donor concentration,  $\text{DH}_0$ , and the rate constants for abstraction,  $k_{\text{abs}}$ , and self-termination,  $k_t$ .

At short extent of conversion of the donor, DH, and DBK, the exponent in eq 4 is small and the expression reduces to:

$$\text{Tot}(t) = \text{DH}_{\text{av}} \left( \frac{k_{\text{abs}}}{\sqrt{k_t}} (\sqrt{\text{BB}(t)} \sqrt{\Delta t}) \right) \quad (5)$$

or

$$k_{\text{abs}} = \frac{[\text{Tot}]}{[\text{DH}_{\text{av}}] \sqrt{\text{BB}} \sqrt{\Delta t}} \quad (6)$$

Short extent of conversion of photoprecursor, DBK, and hydrogen donor DH, results in constant benzyl radical concentration and linear formation of toluene and bibenzyl with duration of photolysis. If DBK is photolyzed at a constant rate of photolysis to short extent of conversion, but the donor DH is appreciably consumed, the time dependence of toluene and bibenzyl production will exhibit curvature described by eq 4. Providing values of  $k_t$  are available for a given solvent system, the method is a particularly convenient method for the determination of rate constants for abstraction,  $k_{\text{abs}}$ , by stabilized radicals from donors.

Experimental rate constants for self-termination of organic free radicals are available from the work of Fischer and coworkers.<sup>6</sup> Rate constants can be estimated using the empirical method recommended by Fischer using the von Smoluchowski equation (eq 7) with diffusion coefficients derived from the Spornol-Wirtz modification of the Debye-Einstein equation (eq 8), or estimated by measurement of the diffusion coefficient of a model of the radical of interest (e.g., toluene for benzyl radical) in the solvent of interest by the Taylor method.<sup>7</sup>

$$2k_t = (8\pi / 1000) \sigma \rho D_{\text{AB}} N \quad (7)$$

$$D_{\text{AB}} = kT / 6\pi \eta f \quad (8)$$

In eq 7,  $N$  is Avogadro's number,  $D_{\text{AB}}$  is the diffusion coefficient of the radical A in solvent B,  $\sigma$  is a spin statistical factor describing the percent of singlet radical encounter pairs formed (1/4) and  $\rho$  is the diameter of the diffusing radical. Eq. 8 is the Spornol-Wirtz (SW)<sup>8</sup> modification of the Debye Einstein equation ( $f = \text{SW microfriction factor}$ ,  $\eta$  is the viscosity of the solvent). A number of the assumptions inherent in this semiempirical approximation are subject to challenge. The assumption that 100% of singlet encounter radical pairs react in the solvent cage, and the assumption that the diffusion constants for the parent hydride can be used as a model<sup>9</sup> for the radical can be challenged. Empirically it has been established by Fischer and coworkers that self-termination rate constants  $k_t$  for small carbon-centered radicals in non-associating solvents

can be estimated with errors less than about 20%. For benzyl radical in alkanes and in toluene, the errors in estimation of the rate constant for self termination of benzyl are less than 15%. Details of the procedure for estimation of values of  $k_t$  have been presented elsewhere. For self-termination of benzyl radical in benzene, the procedure provides the expression:

$$\ln(2k_t/M^{-1}s^{-1}) = 26.94 - 2733/RT, RT \text{ in calories.} \quad (9)$$

The competition kinetic method is most suitable for rate constants in the range  $10^3$ - $10^6 M^{-1}s^{-1}$ .

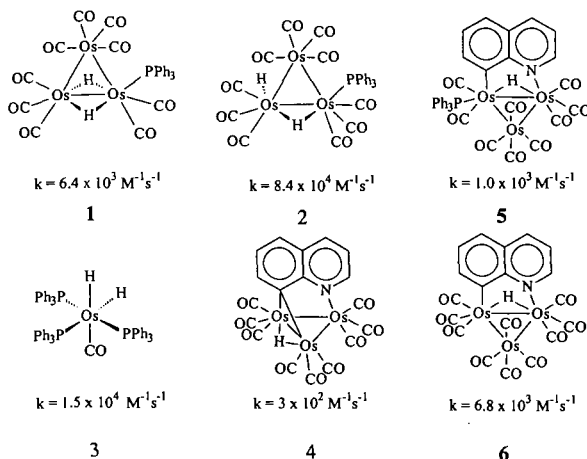
### EXPERIMENTAL APPROACH

Samples of dibenzyl ketone (DBK),  $\sim 0.01 M$ , hydrogen donor,  $10^{-4}$ - $10^{-2} M$ , and internal gas chromatography standard are dissolved in benzene in 5-mm x 6-cm diameter pyrex tubes. The solutions are freeze-thaw degassed in three cycles and sealed on a vacuum line. The samples are temperature-equilibrated in an aluminum block equipped with thermocouples in a temperature-controlled oven equipped with a quartz window to allow photolysis. The samples are photolyzed with the water-filtered light of a 1-kW Hanovia high pressure xenon arc lamp for periods of 0.5 second to typically 30 seconds, to short extent (e.g., < 1-2%) of conversion of DBK and donor. Samples are opened and the yields of toluene and bibenzyl are determined by gas chromatography. Care is taken to ensure that the temperature of the sample remains constant during the photolysis. To verify that equation (6) is appropriate, the time dependence of production of toluene and bibenzyl is measured using constant lamp power levels and carefully reproducible sample positioning. The use of eq 6 is appropriate for linear production of toluene and bibenzyl, as predicted by eqs 1 and 2, where benzyl radical concentration is a constant. For extensive conversion of donor, but constant photolysis rate of the photoprecursor, eq. 4 may be employed. For very fast donors, where significant consumption of donor occurs, very short photolysis times are necessary to operate in the linear range of toluene/bibenzyl concentration. A Uniblitz computer-controlled optical shutter was employed to allow accurate, short photolysis times. Hydrides were synthesized or purchased from Strem Chemical.<sup>10</sup>

### RESULTS AND DISCUSSION

Rate expressions for hydrogen atom abstraction from a selection of osmium mono- and trimetallic clusters were determined, as well as rate constants for ruthenium and rhodium hydrides have been examined. Rate constants for reaction of benzyl radical with metal hydrides in benzene are shown in Figure 1. The immediate observation is that  $\mu$ -bonding does not render the hydrogen atom inaccessible to abstraction by benzyl radical. Structure 1 is only 2-10 times less reactive than  $\sigma$  dihydride 3, and only a factor of ten slower than mixed  $\sigma$ - and  $\mu$ -hydride 2.

**Figure 1.** Hydrogen Abstraction from Mono- and Triosmium hydrides. Rate constants are in benzene at 298K.

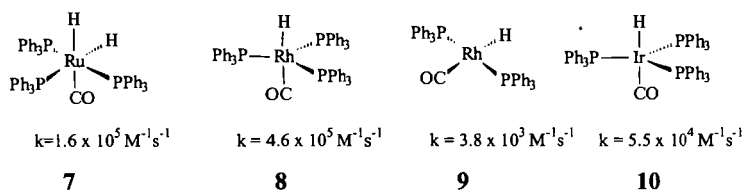


The highly congested and electron deficient structure of 4 results in a rate constant an order of magnitude less than 1. This rate constant is near the practical lower limit of the

termination/abstraction competition kinetic method, due to the formation of trace levels of toluene in the absence of a hydrogen donor. In each of the above cases, steric congestion appears to be an important factor in the observed reaction rates. The reaction of carbon monoxide with **4** results in the formation of electron-precise compound **5** and the rate of hydrogen abstraction increases by a factor of 3. The reaction of compound **4** with a more electron-donating phosphine ligand to form compound **6**, which is analogous in structure to **5** also results in a significant rate increase.

The above rate constants can be compared to the reaction of benzyl radical with ruthenium, rhodium and iridium analogues **7-10**.

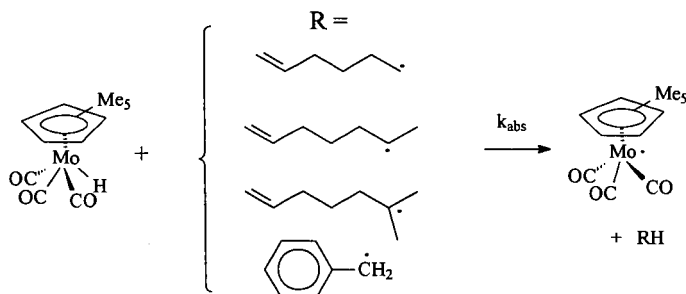
**Figure 2.** Rate Constants, 298 K, for Reaction of Ruthenium and Rhodium Hydrides with Benzyl Radical in Benzene.



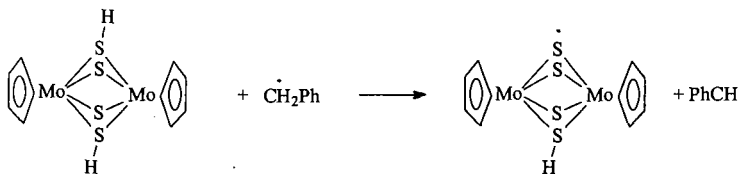
The ruthenium dihydride **7** is an order of magnitude more reactive than the osmium analogue. Square planar 16-electron rhodium hydride **9** is nearly two orders of magnitude slower than 18-electron hydride **8**.

The importance of steric effects in the hydride systems becomes apparent by examination of reactivity trends of transition metal hydrides with alkyl vs. benzyl radical. We have reported<sup>11</sup> a dramatic example of that of the molybdenum hydride,  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ ,  $\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$ . At ambient temperature, the relative reactivity is found, for  $1^\circ : 2^\circ : 3^\circ$  : benzyl (see figure 3), to be 26 : 7.0 : 1 : 1.4 at room temperature. The rate constant for abstraction of hydrogen atom from the molybdenum hydride at room temperature by benzyl radical in benzene is  $1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . By comparison, the reaction of benzyl radical with thiophenol ( $\text{PhSH}$ ) occurs with a rate constant of  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , nearly three orders of magnitude slower than reaction of alkyl radicals with  $\text{PhSH}$ , the relative reactivity of  $1^\circ : 2^\circ : 3^\circ$  alkyl:benzyl radicals is 1:0.9:1:0.027. That is, the molybdenum hydride has much greater selectivity than thiophenol, even though the hydrogen transfer reactions are much more exothermic. This observation underscores the complications in attempting to interpret the kinetic reactivity of the transition metal hydrides.

**Figure 3.** Reactions of Primary, Secondary, Tertiary Alkyl Radicals and Benzyl Radical with  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ .



In related work, we have examined the kinetic reactivity of the thiol (SH) functional group in catalyst prototypes. Kinetic studies of the novel structure **11**<sup>12</sup> in this laboratory have revealed appreciable enhancement of the reactivity of the SH group in hydrogen atom abstraction reactions involving stabilized free radicals (Figure 4). The rate constant for abstraction of hydrogen from the  $\mu$ -SH hydrogen of **11**,  $k_{\text{abs}} = 2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 298K, shows an enhancement by nearly a factor of ten over thiophenol ( $k_{\text{abs}} = 3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ).



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The results illustrate the surprising effects on homolytic reactivity that can be imparted by incorporation of the heteroatom function in the  $\text{Mo}_2\text{S}_4$  cluster.

## CONCLUSIONS

We have presented a preliminary account of characterization of the homolytic kinetic reactivity of a selection of transition metal hydrides, including a selection of triosmium clusters that include  $\sigma$ - and  $\mu$ -bonding of hydrogen to electron-deficient and electron-precise (18-electron) trimetallic clusters, and we have presented new rate constants for reaction of rhodium, ruthenium, iridium and molybdenum hydrides. The results show that  $\mu$ -bonded hydrogen is reduced only moderately in reactivity compared to  $\sigma$ -bonded hydrides for non-fluorinated systems, in which migration of the hydrogen about the triosmium skeleton appears to be slow. The rate constants are sensitive to steric bulk about the cluster, and are sensitive to the degree of electron-deficiency or lack thereof. Work to characterize the reactivity of homolytic intermediates arising from mononuclear and cluster organometallics is underway. Finally, this work has provided quantitative insight into the homolytic reactivity of metal-hydrogen bonding configurations in catalyst intermediates and a view of the enhancement of heteroatom reactivity resulting from incorporation in small clusters.

## ACKNOWLEDGEMENT

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## REFERENCES

- 1 Franz, J.A.; Bushaw, B.A.; and Alnajjar, M.S. *J. Am. Chem. Soc.* **1989**, *111*, 268
- 2 Newcomb, M.; Choi, S.-Y.; Horner, J. H. *J. Org. Chem.* **1999**, *In press*
- 3 (a) Curran, D. P. *Synthesis* **1988**, *6*, 417-39, (b) Baguley, P. A.; Walton, J. C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3072-3082, (c) Davies, A. G. *Organotin Chemistry*; WILEY-VCH: Weinheim, 1997.
- 4 For examples, see (a) Bakac, A. *Inorg. Chem.* **1998**, *37*, 3548-3552, (b) Ash, E. A.; Hurd, P. W.; Darenbourg, M. Y.; Newcomb, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 3313-3317, (c) Bullock, R. M.; Samset, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886-6898, (d) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888-4895, (e) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55-66, (f) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902-7915.
- 5 See, e.g. (a) Alnajjar, M.S. and Franz, J.A. *J. Am. Chem. Soc.* **1992**, *114*, 1052, (b) Autrey, S.T.; Alnajjar, M.S.; Nelson, D.A.; and Franz, J.A. *J. Org. Chem.* **1991**, *56*, 2197.
- 6 (a) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200-266, (b) Lehn, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705-713. (c) Claridge, R. F. C.; Fischer, H. *J. Phys. Chem.* **1983**, *87*, 1960-1967, (d) Huggenberger, C.; Fischer, H. *Helv. Chim. Acta* **1981**, *64*, 338-353.
- 7 See ref. 5b for a detailed description of the procedure for obtaining von Smoluchowski rate expressions.
- 8 Spornol, A.; Wirtz, K., *Z. Naturforsch.* **1953**, *8a*, 522.
- 9 Polarizable radicals may not be well served by this assumption, but benzyl radical is well-behaved: (a) Okamoto, K.; Hirota, N.; and Terazima, M. *J. Chem. Soc. Far. Trans.* **1998**, *94*(2), 185 and *J. Phys. Chem. A* **1997**, *101*, 5269.
- 10 Compounds **1** and **2**: (a) Deeming, A.J.; Hasso, S. J., *J. Organomet. Chem.*, **1975**, *88*, C21. (b) Shapley, J.R., Keister, J.B.; Churchill, M.R., *J. Am. Chem. Soc.*, **1975**, *97*, 4145. (c) Deeming, A.J.; Hasso, S. J., *J. Organomet. Chem.*, **1976**, *114*, 313. Compounds **4**, **5**, and **6**: Kabir, S.E.; Kolwaite, D.S.; Rosenberg, E.; Hardcastle, K.; Cresswell, W.; Gringstaff, J., *Organometallics*, **1995**, *14*, 3611. Arcia, E.; Kolwaite, D.S.; Rosenberg, E.; Hardcastle, K.; Ciurash, J.; Duque, R.; Osella, D.; Gogetto, R.; Milone, L., *Organometallics*, **1998**, *17*, 415. Compound **3**: Ahmad, N.; Levison, J. J.; Roberson, S. D.; Uttley, M. F.; Parshall, G. W. ed., *Inorganic Synthesis*, **1974**, *15*, 54-56. Compound **7**: Ahmad, N.; Levison, J. J.; Roberson, S. D.; Uttley, M. F.; Parshall, G. W. ed., *Inorganic Synthesis*, **1974**, *15*, 48-50. Compounds **8** and **10** purchased from Strem Chemicals.
- 11 Franz, J.A.; Linehan, J.C.; Birnbaum, J.C.; Hicks, K.S.; and Alnajjar, M.S. *J. Am. Chem. Soc.*, submitted.
- 12 Rakowski DuBois, M.; VanDerveer, M.C.; DuBois, D.L.; Haltiwanger, R.C. and Miller, W.K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.